(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
20 March 2003 (20.03.2003)

PCT

(10) Internati nal Publication Number
WO 03/022764 A1

(51) International Patent Classification[7]: C03C 3/068, 13/04

(21) International Application Number: PCT/US02/28573

(22) International Filing Date: 9 September 2002 (09.09.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/317,972 10 September 2001 (10.09.2001) US

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/022764 A1

(54) Title: BISMUTH OXIDE-CONTAINING GLASS COMPRISING POLYVALENT CATIONS

(57) Abstract: This invention relates to a glass containing bismuth oxide that contains polyvalent cations, a process for the production of a glass containing bismuth oxide and its use in optical communications engineering.

Bismuth oxide-containing glass comprising polyvalent cations

This application claims the benefit of priority of U.S. Provisiaonl Patent Application No. 60/317,972, filed September 10, 2001.

Description

This invention relates to a glass containing bismuth oxide that contains polyvalent cations, a process for the production of a glass containing bismuth oxide and its use in optical communications engineering.

Optical amplifier units represent one of the key components of modern optical communications engineering, in particular of WDM technology ("wavelength division multiplexing"). Previously the prior art used mainly quartz glasses doped with optically active ions as the core glass for such optical amplifiers. Amplifiers doped with Er and based on SiO_2 make it possible simultaneously to amplify several closely neighboring channels differentiated by wavelength in the range of 1.5 µm. But because of the only narrow-band emission of the Er in SiO_2 glasses, the latter are not suited for the increasing need for transmission capacity.

Accordingly the need is growing for glasses from which rare earth ions emit in clearly broader bands than from SiO_2 glasses. Here glasses are favored with heavy elements, in particular heavy metal oxide glasses (HMO glasses). Because of their weak

interatomic bonds, these heavy metal oxide glasses have large interatomic electrical fields and thus lead, because of a larger Stark splitting between the normal state and the excited state, to a broader emission of the rare earth ions. Glasses containing bismuth oxide are also proposed as such heavy metal oxides.

But glasses containing bismuth oxide have the drawback that bismuth oxide, under the drastic conditions of the melt, can be reduced by other components. Elementary bismuth that precipitates impairs the optical properties, in particular the transparency, of the glass.

In the prior art, the addition of ceric oxide was proposed to stabilize the high oxidation state of the bismuth (see, e.g., JP 11-317561 and WO 00/23392).

But the addition of ceric oxide is connected with considerable drawbacks. For example, glasses with even slight amounts of less than 0.2 mole % of ceric oxide appear yellowish-orange because the addition of the Ce pushes the UV edge of the glass toward the range of the Er^{3+} emission line at 550 nm. This is also described, for example, in JP 2001-213635 and JP 2001-213636.

To prevent the reduction of bismuth oxide to metallic bismuth even without adding Ce, it is proposed in JP 2001-213636 that the melt temperature be limited to preferably a maximum of 1100°C. But the melt temperature must simultaneously be at least

1000°C. But such a precise control of the melt temperature is not desirable in all cases.

Thus, Thus, an object of this invention is to provide improved glasses containing bismuth oxide and a process for the production thereof.

Upon further study of the specification and appended claims, further objects and advantages of this invention will become apparent to those skilled in the art.

These objects are achieved by the embodiments described herein and in the claims.

In particular this invention relates to glass containing bismuth oxide that has the following composition:

Bi_2O_3	$\geq$ 20 mole %
we can't have? polyvalent cations	0.001-20 mole % (based on oxide)
rare earth compound	0-8 mole % (based on oxide)
other oxides	0-80 mole %.

The glasses according to the invention contain at least one kind of polyvalent cation. It turned out surprisingly that such polyvalent cations can assume the function of stabilizing the high oxidation state of bismuth clearly more effectively than CeO_2. According to this invention, polyvalent cations are, in particular, oxides of the type R_2O_5, for example Nb_2O_5 and/or Sb_2O_5, but also other polyvalent cations such as SnO_2, Cr_2O_3, As_2O_3, V_2O_5. Preferably the glass according to the invention contains oxides of the type R_2O_5, and Sb_2O_5 is especially preferred.

V_2O_5 and/or Cr_2O_3 are less preferred because these polyvalent cations can also discolor the glass. But by experiments it was determined that these polyvalent cations have no absorption in the range of 1.5 µm and thus do not disturb the emission process.

Even slight content of the mentioned components of at least 0.001 mole % based on oxide is enough to prevent the

precipitation of elementary bismuth and thus the degradation of the transparency of the glass. Preferably the content of polyvalent cations is at least 0.005 mole % (based on oxide). But the content of polyvalent cations should not exceed 20 mole %, preferably 10 mole %, based on oxide in each case. One or more of these compounds can be contained in the glass according to the invention and the sum of all polyvalent cations preferably is at least 0.01 mole %, especially preferably 0.1 mole %, based on oxide in each case.

The glass according to the invention contains bismuth oxide in a portion of at least 20 mole %. Preferably the portion of bismuth oxide in the glass is at least 30 mole %. The top limit for bismuth oxide in the glass is preferably 80 mole % since the glass can easily crystallize above this value. More preferably the portion of bismuth oxide is at most 70 mole %, especially preferably at most 60 mole %.

According to one embodiment, the glass containing bismuth oxide comprises at least one rare earth compound as a doping agent. This embodiment relates in particular to the use of the glasses according to the invention as optically active glasses for optical amplifiers and lasers. Preferably the rare earth compound involves at least one oxide, which is selected from oxides of Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and/or Lu. Especially preferred are oxides of the elements Er, Pr, Tm,

Nd and/or Dy.

The glass according to the invention is preferably free of Ce.

Optionally Sc and/or Y compounds can also be contained in the glass according to the invention, in addition to one or more rare earth compounds.

Preferably the rare earth compounds used as doping agents involve so-called "optically active compounds," and "optically active compounds" are understood to be those that lead to making the glass according to the invention capable of stimulated emission when the glass is excited by a suitable pump source.

According to one embodiment, the glass according to the invention is doped with at least two rare earth compounds in a total amount of 0.01 to 15 mole %. Glasses with optically active rare earth ions can be codoped with optically inactive rare earth elements, for example to increase the durations of the emission. Thus, for example, Er can be codoped with La and/or Y. To increase the pump efficiency of the amplifier, Er can, for example, also be codoped with other optically active rare earth compounds such as, for example, Yb. Gd can be codoped to stabilize the crystallization.

Especially preferably the glass according to the invention contains at least Er_2O_3 as the doping agent.

By doping with other rare earth ions such as, for example

Tm, other wavelength ranges can be accessed, as in the case of Tm the so-called S-band between 1420 and 1520 nm. According to other embodiments of this invention, for this reason other rare earth ions such as Tm, Yb, Pr^{3+}, Nd^{3+}, and/or Dy^{3+} can be preferred as the doping agent.

Further, to produce a more effective exploitation of the excitation light, sensitizers such as Yb, Ho and Nd can be added in suitable amounts, for example 0.005-8 mole %.

The content of each individual rare earth compound(s) in the glass is preferably between about 0.005 to 8 mole % based on oxide. According to one embodiment, the content of rare earth compound is between about 2 and 5 mole % based on oxide. According to another embodiment, the content of rare earth compound is about 0.01 to 2 mole % based on oxide.

The glass according to the invention can contain, besides the above-named components, other oxides with a content of 0 to 80 mole %.

Such additional oxides can be contained to adjust physicochemical or optical properties or to lower the tendency to crystallize.

To improve fiber ductility, especially when using the glass according to the invention for an optical fiber amplifier, the addition of at least one conventional network-forming component such as SiO_2, B_2O_3, Al_2O_3, GeO_2, etc., is preferred.

Al_2O_3 in particular can be added to facilitate the formation of glass. Oxides of W and/or Ga can be used to increase the $\Delta\lambda$ value, i.e., to broaden the emissions cross section.

The glass according to the invention contains no gallium- and/or aluminum oxide according to one embodiment.

Further, oxides of elements can be contained that are selected from groups consisting of Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Zn, W, Ti, Zr, Cd and In.

The addition of alkaline oxides is especially advantageous if the glass is to be used for planar application using ion exchange technology. The addition of Li_2O can also be preferred since, in doing so, the glass formation areas are enlarged for glasses containing bismuth oxide. Li_2O is further advantageous if an amplifier with especially good efficiency in the L-band is to be produced.

Optionally the glasses according to the invention can also contain portions of halogenide ions such as F or Cl in a weight portion of about 5 mole %.

The glass according to the invention preferably has the following composition (in mole %):

Bi_2O_3	30-70
polyvalent cations	0.001-8 (based on oxide)
SiO_2	0-60

GeO_2	0-30
B_2O_3	0-60
Al_2O_3	0-50
Ga_2O_3	0-50
In_2O_3	0-30
La_2O_3	0-20
WO_3	0-30
MoO_3	0-30
Nb_2O_5	0-30
Ta_2O_5	0-15
TiO_2	0-30
ZrO_2	0-30
$M^{1}{}_2O$	0-40
$M^{11}O$	0-30
F and/or Cl	0-10
SiO_2 and GeO_2	0.5-60
$B_2O_3+Al_2O_3+Ga_2O_3$	0.5-60
rare earth compound	0-8 (based on oxide)

where M^1 is at least one of Li, Na, K, Rb, Cs, and M^{11} is at least one of Be, Mg, Ca, Sr, Ba and/or Zn.

If the glass according to the invention is used as a so-called passive component, preferably it contains no rare earth compound. But it can be preferred, according to certain

embodiments, that even passive components such as the sheathing of a glass fiber contain slight amounts of optically active cations.

This invention further relates to a process for the production of the glass compound according to the invention.

According to the invention, polyvalent cations are added in a high oxidation state to the glass compound or the batch to be melted. Preferably the polyvalent cations are added to the batch in the highest possible oxidation state. For example antimony should be added to the batch in its pentavalent form, e.g., as $NaSb(OH)_6$. Other such additives are SnO_2, As_2O_3, V_2O_5, Cr_2O_3. These polyvalent cations can be added individually or as a mixture to the batch.

Since antimony, for example, has a higher electron negativity than bismuth, antimony will always oxidize possibly reduced bismuth. On the other hand, antimony is not reduced to the elementary metal, so that the glass cannot become discolored with black by precipitation of elementary metal.

According to one embodiment of the process according to the invention, oxygen can be blown into the glass melt. This so-called oxygen bubbling can support the oxidizing conditions prevailing in the melt.

Further, according to this embodiment of this invention, it is preferred that dry oxygen be blown in. This promotes to a

considerable extent, as a further positive effect, the dehydration of the melt. To dry the glass compound or the melt it is further preferred that the batch of starting materials be thermally pretreated, for example by drying the batch, preferably in a vacuum. The addition of halogenated oxygen also promotes dehydration so that the blowing in of halogenated oxygen is also preferred according to certain embodiments of this invention. These measures for drying the batch or the melt can be used individually or in combination with one another.

This invention further relates to the use of a glass according to the invention for optical amplifiers, and fiber amplifiers or planar amplifiers can be involved. The glass according to the invention can be used in these amplifiers as matrix or core glass and/or sheathing glass. In such glass fibers a compound preferably similar to that of the doping is used as the sheathing glass.

Further, the glass according to the invention can be used as matrix glass and/or as passive component for a laser.

This invention further relates to a glass fiber that contains the glass according to the invention, as well as optical amplifiers that contain a glass fiber according to the invention or the glass according to the invention.

In processing the glass according to the invention as core glass for a fiberlike amplifier, the sheathing glass used

preferably has a very similar composition to the core glass, and the sheathing glass is not doped with an optically active rare earth metal.

In the foregoing and in the following examples, all temperatures are set forth uncorrected in degrees Celsius; and, unless otherwise indicated, all parts and percentages are by weight.

The entire disclosure of all applications, patents and publications, cited above and below, and of corresponding U.S. Provisional Application No.60/317,972, filed September 10, 2001 is hereby incorporated by reference.

Examples

The compounds entered in Table 1 were melted. Non-colored glasses resulted and they were resistant to devitrification.

Table 1

	Example 1	**Example 2**
SiO_2	27.00	14.26
B_2O_3	20.00	28.14
Bi_2O_3	42.00	42.64
Al_2O_3		7.11
Ga_2O_3		7.11
La_2O_3	2.65	
Er_2O_3	0.69	0.40
Yb_2O_3	2.66	
Sb_2O_3	5.00	0.34

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

Claims

1. A glass composition containing bismuth oxide comprising the following (in mole %):

Bi_2O_3	$\geq$ 20 mole %
rare earth compound	0-8 mole % (based on oxide)
polyvalent cations	0.001-20 mole % (based on oxide)
other oxides	0-80 mole %.

2. Glass according to claim 1, wherein the glass contains at least 0.001 to 10 mole % based on oxide of at least one type of polyvalent cation.

3. Glass according to claim 1 or 2, wherein the polyvalent cations are selected from Nb_2O_5, Sb_2O_5, SnO_2, Cr_2O_3, As_2O_3, V_2O_5 and mixtures of these compounds.

4. Glass according to one of the preceding claims, and the glass contains at least one rare earth compound that is selected from oxides of Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and/or Lu.

5. Glass according to one of the preceding claims, wherein the glass contains at least two rare earth compounds.

6. Glass according to one of the preceding claims, wherein at least Er_2O_3 is contained as the rare earth compound.

7. Glass according to one of the preceding claims, wherein the glass contains Sc and/or Y compounds.

8. Glass according to one of the preceding claims that has

the following composition (in mole %):

Bi_2O_3	30-80
SiO_2	0-60
GeO_2	0-30
B_2O_3	0-60
Al_2O_3	0-50
Ga_2O_3	0-50
In_2O_3	0-30
WO_3	0-30
MoO_3	0-30
La_2O_3	0-20
Nb_2O_5	0-30
Ta_2O_5	0-15
TiO_2	0-30
ZrO_2	0-30
$M^1{}_2O$	0-40
$M^{11}O$	0-30
F and/or Cl	0-10
SiO_2 and GeO_2	0.5-60
$B_2O_3+Al_2O_3+Ga_2O_3$	0.5-60
rare earth compound	0.005-8 (based on oxide)

where M^1 is at least one of Li, Na, K, Rb, Cs, and M^{11} is at least one of Be, Mg, Ca, Sr, Ba and/or Zn and wherein the sum of all polyvalent cations is at least 0.01 mole % based on oxide.

9. Process for the production of a glass according to one of claims 1 to 8, wherein at least one type of polyvalent cation is added in a highly oxidized state to the batch to be melted.

10. Process according to claim 9, wherein Nb_2O_5, Sb_2O_5, SnO_2, Cr_2O_3, As_2O_3, V_2O_5 and mixtures of these compounds are added as polyvalent cations in a portion of at least 0.001 mole %.

11. Process according to claim 9 or 10, wherein Sb(V) is added in the form of $NaSb(OH)_6$.

12. Use of a glass according to one of claims 1 to 8 as matrix glass for optical amplifiers.

13. Use of a glass according to claim 12, wherein the optical amplifier is a fiberlike amplifier.

14. Use according to claim 12, wherein the optical amplifier is a planar amplifier.

15. Use of a glass according to one of claims 1 to 8 as matrix glass for a laser.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/28573

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C3/068 C03C13/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 127 858 A (ASAHI GLASS CO LTD) 29 August 2001 (2001-08-29) cited in the application paragraph '0014! figures 6,7 example 7; table 2 ---	1-6, 8-10, 12-14

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search	Date of mailing of the international search report
30 January 2003	06/02/2003

Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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